Appl. Phys. A 74 [Suppl.], S634–S636 (2002) / Digital Object Identifier (DOI) 10.1007/s003390201350

Applied Physics A
Materials
Science & Processing

Spin excitations in 3D molecular magnets probed by neutron scattering

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Received: 18 July 2001/Accepted: 8 January 2002 –

Abstract. The emerging field of molecular magnetism constitutes a new branch of materials science that deals with the magnetic properties of molecules, or assemblies of molecules, that contain magnetic centers. The growing interest in understanding the origin of the magnetic ordering in these materials is to obtain novel multiproperty molecular magnetic materials with high transition temperatures. Molecules based on the dicyanamide ion [N≡C–N–C≡N], abbreviated (dca), such as $M(dca)_2$ [M = Mn, Ni], have shown interesting bulk properties that prompted our inelastic neutron scattering (INS) studies. While the Mn^{2+} ion is isotropic because of its $L = 0$ configuration, the isostructural Ni analog has $S = 1$ and demonstrates marked single-ion anisotropy. $Mn(dca)_2$ is a canted antiferromagnet below 16 K, while $Ni(dca)_2$ is a ferromagnet below 21 K. INS has been used to investigate the magnetic excitations in $Mn(dca)_2$ and $Ni(dca)_2$. For $Mn(dca)_2$, a Heisenberg model gives good correspondence with the experimental results.

PACS: 78.70.Nx; 75.30.Ds; 71.70.Gm

The design, characterization, and development of engineering materials with both optoelectronic and magneto-optical properties is one of the current stimulating fields of research for chemists and physicists [1]. Due to the enormous flexibility and power that classical molecular chemistry provides in the design of new multiproperty materials, major breakthroughs are expected. In the last few years, several families of molecular-based magnets showing a variety of phenomena such as spontaneous magnetization with ordering temperatures ranging from a few kelvins to 350 K [2], photoinduced magnetism [3], and metamagnetism [4] have already been developed. Of particular interest is the family of metal-dicyanamides, $M(dca)_2$ (M = Mn, Fe, Co, Ni, Cu, Cr), which exhibit either ferromagnetism or canted antiferromagnetism with high coercive fields (~ 1.78 T), comparable to that of permanent magnets such as Sm–Co or RE–Nd–B [5].

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The magnetic phase diagrams of the metal-dicyanamides have been obtained by a combination of DC magnetization, AC susceptibility, specific heat, and neutron diffraction [6]. Neutron powder diffraction studies [7, 8] show that these compounds are isostructural, adopting an orthorhombic form of the rutile structure, similar to $CrCl_2$ and CuF_2, having a space group *Pnnm* with $Z = 4$. A zero-field splitting is expected to be a common feature of these systems due to the axial distortion of the octahedra surrounding the metal ions. Nonetheless, the environment around each of the two metal ions, with axial elongation and opposite tilting of the octahedra in each unit cell, affect the resulting magnetic structure. For instance, below 16 K, $Mn(dca)_2$ (d^5, $S = 5/2$) is an antiferromagnet with the magnetic moments ($\mu(Mn^{2+}) = 4.61(1)\,\mu_B$) of the two Mn ions slightly tilted (5 degrees) from the *a* axis [7]. The ground state is ferromagnetic for the Ni compound. Below its ordering temperature ($T_c = 21$ K) the spins are collinear with a magnetic moment of $2.21\,\mu_B$ oriented along the *c* axis [8].

Information about the exchange interaction of the 3*d* transition-metal ions is usually obtained from the temperature dependence of the magnetic susceptibility. However, when anisotropy becomes important, or the size of the magnetic cluster increases, a susceptibility curve does not contain enough information and a combination of several techniques is necessary. Inelastic neutron scattering (INS) is the most powerful tool used to investigate spin excitations and has proved to be valuable in measuring magnetic exchange and anisotropy in the study of rare-earth and transition-metal ions [9]. Here we present INS results in an energy range up to 15 meV for Mn and $Ni(dca)_2$; a qualitative analysis of the observations is proposed based on single-ion anisotropy. Results obtained on the disk chopper spectrometer (DCS) at the National Institute of Standards and Technology (NIST) clearly shows a spin wave emerging from the antiferromagnetic zone center in $Mn(dca)_2$. The excitation reaches a maximum energy of 1.3 meV that follows the magnetic scattering form factor along $\boldsymbol{Q}$. Furthermore, the DCS can be used to obtain some dispersion information of magnetic interactions even in powdered samples.

1 Experimental details

Approximately 15 g of Mn and $Ni(dca)_2$ were prepared as described elsewhere [8, 10]. The crystal structures were verified on the neutron powder diffractometer 'special environment powder diffraction' (SEPD) at the Intense Pulsed Neutron Source (IPNS). The polycrystalline sample was then sealed under helium in an aluminum container suitable for the INS experiments. For the Mn sample, cold-neutron spectra were recorded on the high-resolution DCS at the NIST Center for Neutron Research. The measurements were performed at temperatures between 8 and 50 K using incident wavelengths of 4.8 Å and 6 Å, and the resolution at zero energy transfer half width half maximum (HWHM) was 60 and 30 μeV, respectively. In the case of the Ni sample, INS measurements were performed at IPNS using the low-resolution medium-energy spectrometer (LRMECS) between 10 and 150 K, using an incident energy of 15 meV with an elastic resolution HWHM = 0.5 meV.

The data treatment involved subtraction of a background spectrum obtained from an empty sample can and absolute unit conversions were performed by measuring the elastic incoherent scattering from a vanadium standard under the same experimental conditions. The time-of-flight spectra were converted to energy distributions, corrected for the energy dependence of the detector efficiency, and plotted against energy transfer using standard programs available at NIST and IPNS.

2 Spin excitations in molecular magnets

In Fig. 1a we present the INS spectra of $Mn(dca)_2$ obtained on the DCS with an incident wavelength of 4.8 Å, 3.55 meV. Below T_N (16 K) we observe one prominent inelastic transition at 1.3 meV. As the temperature increases, and the system becomes paramagnetic, the excitation disappears.

Further evidence that the scattering is magnetic in origin is provided in $S'(Q, \omega)$. Figure 1b shows that, in the antiferromagnetic (AFM) phase, the low-energy spectral weight decreases with increasing Q, as expected for magnetic scattering. We can also clearly observe the periodicity of the excitation. The band of magnetic scattering at 1.3 meV exhibits a peak as a function of $|Q|$ centered at 0.7 $Å^{-1}$ with a HWHM = 0.15 $Å^{-1}$. This indicates that the excited state involves AFM nearest-neighbor correlations.

The scattered intensity from $Ni(dca)_2$ above and below T_c (21 K) is shown in Fig. 1c with an incident neutron energy of 15 meV. We observe a well-resolved near-dispersionless magnetic excitation at about 3.9 meV.

To understand our results we do not consider the ground-state properties of the material, but rather the description of the excitations that arise from coherent precessions of the spins about their mean values. Spin-wave theory gives an extremely good description of these excitations [11, 12]. For an extended system with small anisotropy the dispersion relation for a spin wave, expressed in terms of the effective exchange and anisotropy fields H_E and H_A, is given by

$$\hbar\omega(q) = \gamma\hbar \left[(2H_E + H_A) H_A + H_E^2 \left(1 - \Gamma_q\right)^2 \right]^{1/2} , \qquad (1)$$

where $H_E = SzJ/\mu_B$, S is the spin value (5/2 for Mn^{2+} and 1 for Ni^{2+}), J is the magnetic exchange interaction between the first nearest neighbors (z), $H_A = SD/\mu_B$, D is the zero-field splitting parameter, and $\Gamma_q = (1/z) \sum \exp i\, \boldsymbol{q} \cdot \boldsymbol{r}$. Thus, considering that $H_A \ll H_E$, $H_A/H_E \sim 10^{-3}$ (which is comparable to the ratio for MnF_2), a preliminary analysis of the

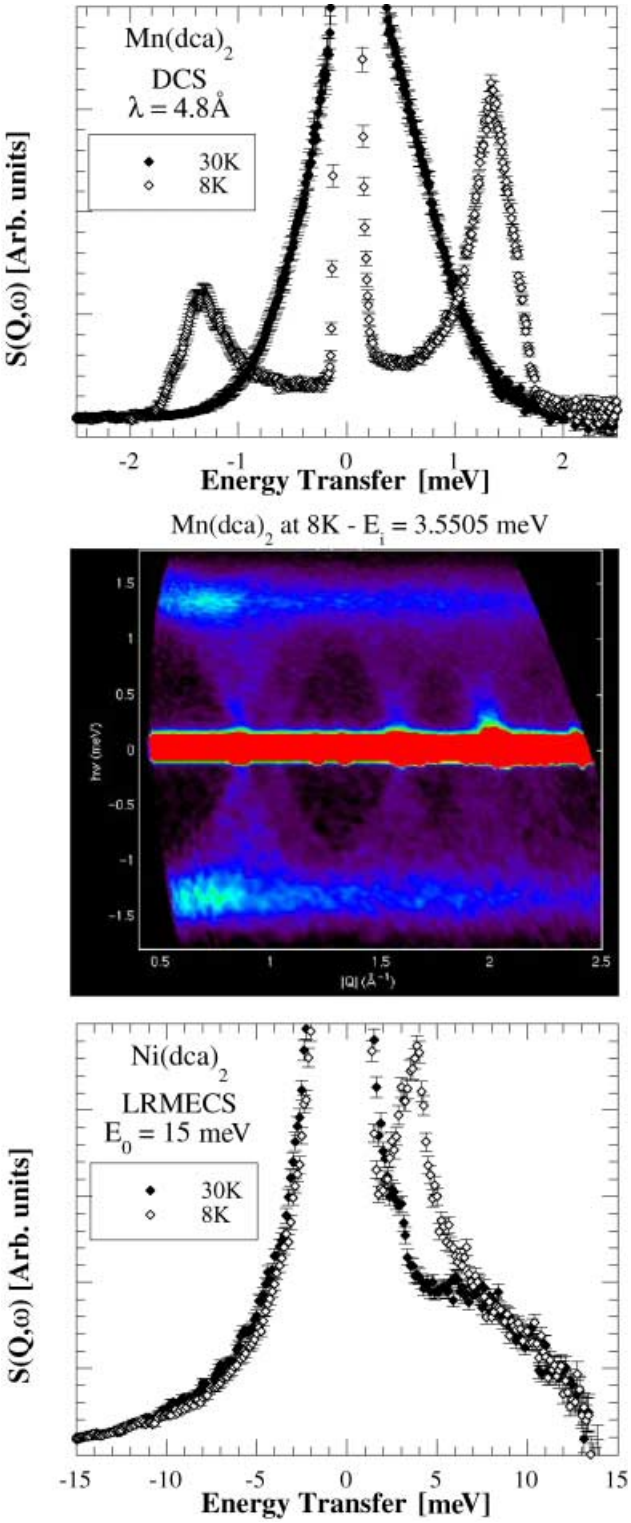

Fig. 1. **a** Temperature dependence of the magnetic excitation in $Mn(dca)_2$ measured with the DCS with $\lambda = 4.8$ Å, $|\boldsymbol{Q}| = 1.5$ $Å^{-1}$. **b** Energy–momentum spectrum obtained at 8 K using the DCS, clearly showing the spin-wave dispersion. **c** Temperature dependence of the magnetic excitation in $Ni(dca)_2$ measured with the LRMECS with $E_0 = 15$ meV, $|\boldsymbol{Q}| = 1$ $Å^{-1}$

$Mn(dca)_2$ data has been performed using the parameters J and D previously reported [7]. We obtain

$$\hbar\omega_{\min}(\mathrm{Mn(dca)_2}) = \langle S\rangle\sqrt{2JD} = 6\times10^{-4}\,\mathrm{meV}\,, \quad (2)$$

$$\hbar\omega_{\max}(\mathrm{Mn(dca)_2}) = \langle S\rangle(zJ+D) = 1.18\,\mathrm{meV}\,. \quad (3)$$

These findings are in very good agreement with the experimental results, indicating that $Mn(dca)_2$ can be described using mean-field and Heisenberg models. Furthermore, combining our data obtained using DCS and numerical calculations, information about the dispersion of the magnetic interactions could be obtained [13].

Now we turn to $Ni(dca)_2$. While the energy of the magnetic excitation decreases with increasing temperature, its line width seems to be resolution-limited [14]. On the other hand, the evolution of the magnetic peak position as a function of momentum transfer revealed no pronounced $\boldsymbol{Q}$ dependence, which may suggest evidence of single-ion anisotropy.

3 Summary

To date, neutron scattering has hardly ever been used to investigate the properties of molecular magnets. Here we have used a new high-resolution DCS that made possible the observation of spin-wave dispersion lines in a powder sample. Our results demonstrate that the Heisenberg model is an excellent starting point for describing the magnetic interactions in $Mn(dca)_2$. Moreover, INS proved to be invaluable for a detailed understanding of the interplay of exchange and anisotropy in the 3D molecular-based magnet. Further experimental (neutron and Raman scattering) and theoretical studies are under way in order to explain the variations of the magnetic configurations in the $M(dca)_2$ family.

Acknowledgements. The authors would like to thank Nicole Murphy for setting up the LRMECS experiments. Argonne National Laboratory is funded by the U.S. DOE-BES under Contract No. W-31-109-ENG-38. Identification of commercial equipment in the text is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology.

References

1. O. Kahn: *Molecular Magnetism* (VCH, New York 1993)
2. J.M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein, J.S. Miller: Science **252**, 1415 (1991)
3. D.A. Pejakovic, J.L. Manson, J.S. Miller, A.J. Epstein: Phys. Rev. Lett. **85**, 1994 (2000)
4. H.-Z. Kou, S. Gao, B.-W. Sun, J. Zhang: Chem. Mater. **13**, 1431 (2001)
5. M. Kurmoo, P. Day, C.J. Kepert: *Supramolecular Engineering of Synthetic Metallic Materials* (Kluwer, Dordrecht 1999)
6. C.R. Kmety, J.L. Manson, Q.-Z. Huang, J.W. Lynn, R.W. Erwin, J.S. Miller, A.J. Epstein: Mol. Cryst. Liq. Cryst. **334**, 631 (2000)
7. C.R. Kmety, Q.-Z. Huang, J.W. Lynn, R.W. Erwin, J.L. Manson, S. McCall, J.E. Crow, K.L. Stevenson, J.S. Miller, A.J. Epstein: Phys. Rev. B **62**, 5576 (2000)
8. C.R. Kmety, J.L. Manson, Q.-Z. Huang, J.W. Lynn, R.W. Erwin, J.S. Miller, A.J. Epstein: Phys. Rev. B **60**, 60 (1999)
9. H.U. Gudel: *Molecular Magnetism: From Molecular Assemblies to Devices* (Kluwer, Dordrecht 1996)
10. J.L. Manson, C.R. Kmety, Q.-Z. Huang, J.W. Lynn, G. Bendele, S. Pagola, P.W. Stephens, A.J. Epstein, J.S. Miller: Chem. Mater. **10**, 2552 (1998)
11. W. Marshall, S.W. Lovesey: *Theory of Thermal Neutron Scattering* (Oxford University Press, London 1971)
12. G.T. Rado, H. Suhl (eds.): *Magnetism* (Academic, New York 1965)
13. T. Yildirim et al.: in preparation
14. H.N. Bordallo et al.: in preparation. Based on new results obtained using SPINS at NIST, a complete softening is observed at T_N. Further details will be given in a future publication